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# $ZrOCl_2 \cdot 8H_2O$ as an efficient catalyst for the synthesis of dibenzo [*b*,*i*]xanthene-tetraones and fluorescent hydroxyl naphthalene-1,4-diones

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**Abstract** An efficient and environmentally benign protocol for the synthesis of dibenzo [*b*,*i*]xanthene-tetraones and fluorescent hydroxyl naphthalene-1,4-diones in the presence of a catalytic amount of $ZrOCl_2 \cdot 8H_2O$ as an inexpensive and eco-friendly catalyst with high catalytic activity under solvent-free conditions is reported.

**Keywords** Dibenzoxanthene · Hydroxyl naphthalene-1,4-diones · $ZrOCl_2$ · Solvent-free

## Introduction

The use of zirconium(IV) salts as an efficient Lewis acid for various transformations has been well documented in the literature, because of their easy availability, moisture stability, and low toxicity [1–3]. Among the various types of Zr(IV) salts, $ZrOCl_2 \cdot 8H_2O$ in particular has the advantages of moisture stability, readily availability, and easy handling [2]. Also, the low toxicity of $ZrOCl_2 \cdot 8H_2O$ is evident from the LD50 [LD50 ($ZrOCl_2 \cdot 8H_2O$, oral rat) = 3,500 mg/kg] [3]. Therefore, the application of $ZrOCl_2 \cdot 8H_2O$ in organic synthesis is of renewed interest.

It has been well known for many years that dyes have been most widely used in dyeing, as well as in high technology as such as lasers, liquid crystalline displays, electro-optical devices, and ink-jet printers [4, 5]. Xanthene derivatives occupy an important position among different families of dyes, owing to a number of reasons related to their photochemical and photophysical properties [6]. Rose Bengal, Eosin, and other xanthene dyes are the most frequently employed dye-sensitizers when a

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quantitative interpretation of the photodynamic effect is required [7]. In recent years, a number of analyte sensors have been designed using these scaffolds via synthesis of new xanthene-based dyes [8]. Furthermore, xanthenes have been reported to possess diverse biological and therapeutic properties such as antibacterial, antiviral, and anti-inflammatory activities, as well as being used in photodynamic therapy [9, 10].

Fluorescent heterocyclic compounds are of interest in many disciplines as, e.g., emitters for electroluminescence devices [11], molecular probes for biochemical research [12], in traditional textile and polymer fields [13], fluorescent whitening agents [14], and photo-conducting materials [15]. Quinone derivatives have been reported as fluorescence compounds [16–19]. On the other hand, molecules with the quinone structure constitute one of the most interesting classes of compounds in organic chemistry, due to their biological properties, their industrial applications, and their potential as intermediates in the synthesis of heterocycles [20].

As part of our research aimed at developing new methods for organic transformations [21–24], and due to the unique advantages of $ZrOCl_2 \cdot 8H_2O$, the aim of our research described here was to develop the synthesis of dibenzo[*b*,*i*]xanthene-tetraones and fluorescent hydroxyl naphthalene-1,4-diones employing $ZrOCl_2 \cdot 8H_2O$ as an efficient and mild Lewis acid catalyst.

## Experimental

### General procedure for the synthesis of 3

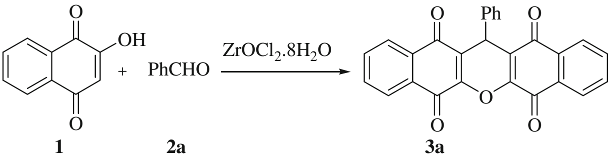
A mixture of 2-hydroxynaphthalene-1,4-dione (2 mmol), aldehydes (1 mmol), and $ZrOCl_2 \cdot 8H_2O$ (20 mol %) was stirred at 100 °C for an appropriate time (the progress of the reaction was monitored by TLC). After completion, the precipitated reaction mixture was washed with $H_2O$ (5 ml) and EtOH (5 ml) to afford the solid pure product **3**. The catalyst was separated from the precipitated reaction mixture simply by washing with water and EtOH, and reused after washing with $CH_2Cl_2$ and drying at 60 °C.

### General procedure for the synthesis of 5

A mixture of 2-hydroxynaphthalene-1,4-dione (1 mmol), aldehydes (1 mmol), amines (1 mmol) and $ZrOCl_2 \cdot 8H_2O$ (20 mol %) was stirred at 100 °C for an appropriate time (the progress of the reaction was monitored by TLC). After completion, the precipitated reaction mixture was washed with $H_2O$ (5 ml) and EtOH (5 ml) to afford the solid pure product **5**. The catalyst was separated from the precipitated reaction mixture simply by washing with water and EtOH, and reused after washing with $CH_2Cl_2$ and drying at 60 °C.

All the products are known and were fully characterized by a comparison with authentic samples (melting point) and IR spectra [22, 24].

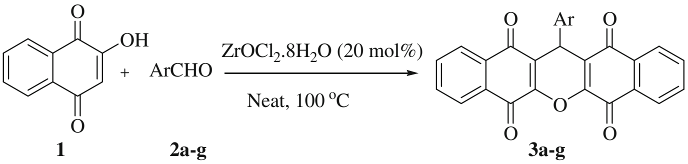
**Table 1** Screening of the reaction conditions



| Entry | Solvent | $ZrOCl_2 \cdot 8H_2O$ | Time (h) | Yield (%) |
|---|---|---|---|---|
| 1 | EtOH (Reflux) | 20 mol% | 10 | 45 |
| 2 | $CHCl_3$(Reflux) | 20 mol% | 10 | Trace |
| 3 | $CH_3CN$(Reflux) | 20 mol% | 10 | <30 |
| 4 | S.F. (100 °C) | 20 mol% | 6 | 84 |
| 5 | S.F. (100 °C) | 25 mol% | 6 | 83 |
| 6 | S.F. (100 °C) | 15 mol% | 6 | 75 |
| 7 | S.F. (80 °C) | 20 mol% | 6 | 65 |
| 8 | S.F. (100 °C) | 0 | 6 | <30 |

*S.F.* Solvent-free

**Table 2** Synthesis of dibenzoxanthene-tetraones **3**



| Product **3** | Ar | Time (h) | Yield (%) |
|---|---|---|---|
| a | $C_6H_5$ | 6 | 84 (82.80)[a] |
| b | $4\text{-}Cl\text{-}C_6H_4$ | 6 | 81 |
| c | $4\text{-}Br\text{-}C_6H_4$ | 6 | 79 |
| d | $4\text{-}F\text{-}C_6H_4$ | 6 | 82 |
| e | $4\text{-}Me\text{-}C_6H_4$ | 7 | 79 |
| f | $2\text{-}Cl\text{-}C_6H_4$ | 6.5 | 80 |
| g | $3\text{-}NO_2\text{-}C_6H_4$ | 6 | 90 |

[a] Isolated yield after recycling of catalyst

## Results and discussion

Initially, the reaction of 2-hydroxynaphthalene-1,4-dione **1** (2 mmol) and benzaldehyde **2a** (1 mmol) as a simple model substrate in the presence of $ZrOCl_2 \cdot 8H_2O$ in different solvents and under solvent-free conditions was investigated to optimize the reaction conditions. It was found that the reaction under solvent-free conditions at 100 °C after 6 h resulted in a higher isolated yield (Table 1). Similarly, the molar ratio of $ZrOCl_2 \cdot 8H_2O$ was studied with the optimum amount being 20 mol % (entry 4). When this reaction was carried out without $ZrOCl_2 \cdot 8H_2O$, the yield of the expected product was a trace (entry 8).

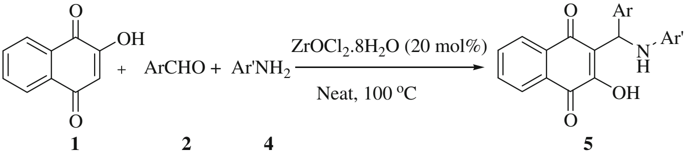
Using the optimized conditions, the generality of this reaction was examined using several types of aromatic aldehydes **3a–h**. In all cases, the reactions gave the corresponding products in good isolated yields (Table 2).

Another advantage of this approach could be related to the heterogeneous catalytic process under solvent-free conditions and the reusability of catalyst. We found that the catalyst could be separated from the reaction mixture simply by washing with water and reusing after washing with $CH_2Cl_2$ and drying at 60 °C. The reusability of the catalyst was checked by the reaction of 2-hydroxynaphthalene-1,4-dione **1** and benzaldehyde **2a** under optimized reaction conditions. The results showed that the catalyst can be used effectively three times without any loss of its activity (Table 2, entry 1). Therefore, the recyclability of catalyst makes the process economical and potentially viable for commercial applications.

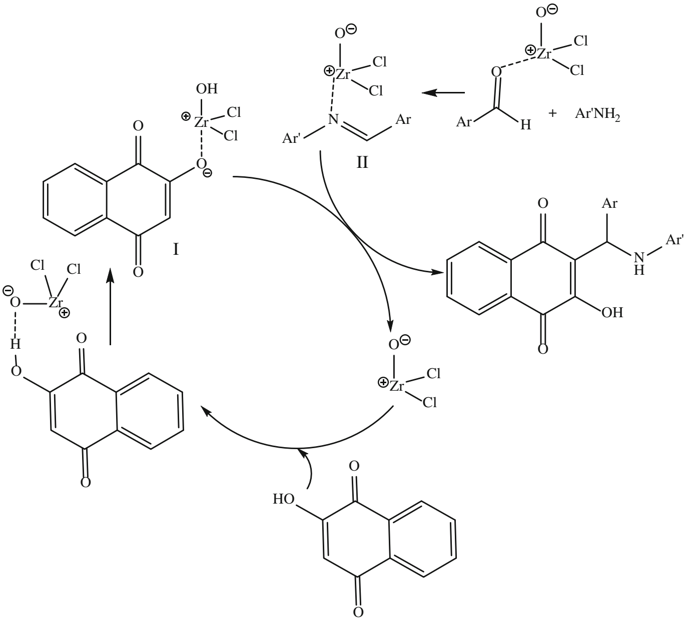
To further explore the potential of $ZrOCl_2 \cdot 8H_2O$, we investigated the reaction of 2-hydroxynaphthalene-1,4-dione **1** and aldehydes **2** with aromatic amines **4** and obtained fluorescent hydroxyl naphthalene-1,4-dione derivatives **5** in good isolated yields under the same reaction conditions (Table 3).

The proposed mechanism involves the attack of in situ-generated enolate I on the in situ-generated aldimine II as shown in Scheme 1 [25]. $ZrOCl_2$, used in catalytic amounts, is recycled in the reaction.

**Table 3** Synthesis of hydroxyl naphthalene-1,4-diones **5**



| Product **5** | Ar | Ar′ | Time (h) | Yield (%) |
|---|---|---|---|---|
| a | $C_6H_5$ | $C_6H_5$ | 7 | 88 |
| b | 4-Me–$C_6H_4$ | $C_6H_5$ | 7 | 80 |
| c | 4-OH–$C_6H_4$ | $C_6H_5$ | 7 | 81 |
| d | 4-$NO_2$–$C_6H_4$ | $C_6H_5$ | 7 | 85 |
| e | $C_6H_5$ | 4-Me–$C_6H_4$ | 9 | 85 |
| f | 4-MeO–$C_6H_4$ | 4-Me–$C_6H_4$ | 8 | 84 |
| g | 4-Me–$C_6H_4$ | 4-Me–$C_6H_4$ | 9 | 83 |
| h | 4-OH–$C_6H_4$ | 4-Me–$C_6H_4$ | 9 | 86 |
| i | 4-$NO_2$–$C_6H_4$ | 4-Me–$C_6H_4$ | 7 | 79 |
| j | 2-Cl–$C_6H_4$ | 4-Me–$C_6H_4$ | 7 | 87 |



**Scheme 1** Proposed mechanism for the synthesis of **5**

## Conclusion

In conclusion, we have demonstrated that $ZrOCl_2·8H_2O$ can be used as a green and reusable catalyst for the efficient synthesis of dibenzo [*b*,*i*]xanthene-tetraones and fluorescent hydroxyl naphthalene-1,4-diones under solvent-free conditions. Moreover, the cheapness, easy availability of the reagent, and easy and clean workup make this method attractive for organic chemists.

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